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A technical and economical evaluation of CO_2 capture from FCC units

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Abstract

The present work was focused on a technical and economical evaluation of two distinct CO_2 capture technologies applied to an FCC unit, namely amine absorption and oxyfired FCC. All capital costs, utility requirements and chemical consumption of each technology were determined in order to allow the calculation of CO_2 capture and avoided costs. The results showed a 45% decrease in CO_2 capture cost for oxyfiring technology compared to the amine absorption alternative. As for the technical feasibility of oxyfiring in the FCC regenerator, a series of bench and pilot plant scale tests were performed. Product profile, stability of operation and the effectiveness of coke burn were evaluated. No significant changes from normal operation were observed.

*Keywords:*FCC; CO_2 capture; Oxyfiring; Oxycombustion

1. Introduction

The oil refining industry is one of the most significant sources of greenhouse gas (GHG) emissions, with considerable contribution from downstream activities. Moreover, the fluid catalytic cracking process (FCC) is one of the main sources of greenhouse gas emissions (mainly CO_2) in the oil refining industry as an isolated source (stack emission). The CO_2 emission from FCC units may represent as high as 40 – 45% of total refinery emissions. Capturing CO_2 from FCC flue-gas is therefore an important step in mitigating the CO_2 emission of the refinery as a whole.

The conventional catalytic cracking process converts heavy oil fractions to lighter products such as liquid petroleum gas (LPG) and gasoline with the use of a cracking catalyst. During the reaction step, coke is also formed and deposited on the surface of the catalyst, which is then deactivated. To reestablish catalyst activity, coke is

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burned in the regenerator with the use of air, thus forming CO_2, which is present in the flue-gas at typical concentrations of 10 – 20% vol. (full combustion).

Based on the characteristics of the FCC process, two possible ways to capture CO_2 from FCC include post-combustion technologies, such as CO_2 absorption, as well as oxyfiring, with the substitution of air by pure O_2 in the regeneration step. In this later configuration, some of the captured CO_2 is recycled back to the regenerator mainly to prevent temperature runaways during the combustion reaction. In this way the excess N_2 injected with air in the conventional mode is avoided and the separation of N_2 from produced CO_2 is not required. However an air separation unit (ASU) is required to produce the oxygen. The oxyfiring concept has been previously described in literature for coal gasification as well as for FCC processes [1, 2].

The main objective of the present work was to evaluate both technological options for CO_2 capture in FCC units. A direct comparison between post-combustion and oxyfiring technologies was performed including cost estimates for each of the process schemes. This part of the work was performed within the scope of the Carbon Capture Project – Phase 2 (CCP-2). Furthermore, a series of bench and pilot plant tests were performed to evaluate the technical viability of applying the oxyfiring concept on an FCC unit.

2. Study basis for economic evaluation

An amine scrubber unit for CO_2 absorption was taken as the post-combustion technology option and chosen to be the base case of the study since it is considered a commercially proven technology. In this case, no changes in FCC operation are necessary as opposed to the oxyfiring alternative. For the study, an existing 10,000 m^3/d resid FCC unit was taken as reference. Based on process data collected from the unit, mass and energy balance calculations were made to estimate the flue-gas composition for the FCC unit operating in the oxyfiring mode, considering two oxygen purity levels: 99.5% and 95%. The flue-gas composition for the base case and both oxyfiring conditions are shown in Table 1.

Table 1 – Flue-gas composition

	Base case	Oxyfiring	
		99.5% O_2	**95% O_2**
Total flow-rate (t/h)		765 666	755 170
O_2 (%mol.)	2.7	2.8	2.8
CO_2 (%mol.)	13.5	89.4	84.3
H_2O (%mol.)	10.0	6.95	6.98
N_2 (%mol.)	72.90	0.17	1.71
Ar (%mol.)	0.85	0.40	3.99
CO (ppm)	9.0	9.0	9.0
SOx (ppm)	378	2383	2246
NOx (ppm)	81	536	505

The CO_2 product specification (table 2), which was used to define the purification processes, was established as suggested by CCP-2, taking into account the final use of CO_2 for enhanced oil recovery (EOR). A minimum of 90% CO_2 recovery should also be achieved in each process. The only specification for the recycle stream was a 3%vol. H_2O limit to avoid an increased catalyst deactivation in the regenerator.

For the oxyfired cases, the CO_2 recycle rate was established to maintain the same volume flow-rate as that of N_2 in air. This was done so that O_2 concentration in the gases entering the regenerator in the oxyfiring cases would be the same as that of base case (when air is used).

Table 2 – CO_2 product specification

Component	Specification	Component	Specification
CO_2	> 95%	**NO_x**	no spec
H_2O	< 50 ppm	**Inerts**	< 4 mol%
SO_2	no spec	**O_2**	< 3 mol%
Pressure	150 bar g	**Temperature**	< 60 ^oC

3. Results and discussion of economical evaluation

3.1. Process calculations

The process flow diagrams for the purification of CO_2 in each case studied are presented in Figures 1 - 3. In all cases, the hot flue-gas passes through a waste heat steam generator (WHSG) for high pressure steam generation and then through the SOx removal scrubber, which brings SOx levels down to 7 ppmv. The CO_2 compression and dehydration systems are also common to each case to meet the water and pressure specifications of the CO_2 product. The base case requires an amine plant whereas the oxyfired cases require an air separation unit (ASU). The 95% O_2 case further requires a propane refrigeration system to concentrate the CO_2 to meet the 95% CO_2 specification.

The amine plant considered for this study uses the Kerr-McGee CO_2 recovery technology, which basically uses an aqueous solution of MEA to absorb CO_2, which is then regenerated by the application of heat (from low pressure steam). The dehydration of the CO_2 is accomplished by compression and cooling, followed by molecular sieve drying, composed of two vessels operating in an adsorption/regeneration cycle. The water specification in the exiting gas is less than 50 ppmv. For the base case, the main purpose of the SOx scrubber was to bring the SO_2 concentration down to 7 ppmv to allow a successful operation of the amine plant. As for the oxyfired cases, the SOx scrubber was also used to prevent sulfur poisoning of the molecular sieve beds and to prevent eventual SO_2 emission upon the regeneration of the beds.

The main process results calculated in each of the cases studied are presented in Table 3. The CO_2 purity was greater for the base case since it is an intrinsic characteristic of the absorption technology applied due to the high selectivity of the MEA solution towards CO_2. On the other hand CO_2 recovery was lower, although it was above the specified limit. It is important to emphasize that the process conditions were not necessarily optimized. The 95% oxyfired case recovery was less than the 99.5% oxyfired case because some of the CO_2 was vented to the atmosphere in the flash tank to meet the 95% purity requirement.

3.2. Utility demands and chemical requirements cost

All utility requirements and power demand were estimated and the values may be seen in Table 4. All drivers needed for new equipment were assumed to be electric motors. No energy integration/optimization was considered in this study. Therefore all steam consumed was assumed to be “imported” from the refinery whereas the high pressure (HP) steam produced in the WHSG was “exported” back to the refinery. Although the air blower is an existing equipment piece and was not included in the total capital cost estimates for the base case, the high pressure steam consumed in its steam turbine driver has been considered in the utility requirements estimates. This was done so the comparison between the different technologies could be made on the same basis since, for the oxyfiring cases, the air blower is replaced by the CO_2 recycle compressors. The major differences between the post-combustion and oxyfiring technologies are related to the steam/power balance. While in the base case there is a great steam requirement for the air blower steam turbine (HP) and amine plant regeneration step (low pressure – LP), the oxyfiring technologies demand greater power supply for the ASU as well as for the recycle compressors.

Table 3 – Process results

	Units	Base Case	99.5%O_2	95%O_2
CO_2 Purity	vol%	99.95	96.07	95.24
CO_2 Recovery	%	90.42	99.99	90.52
Product CO_2	ton/h	101.7	112.3	101.6

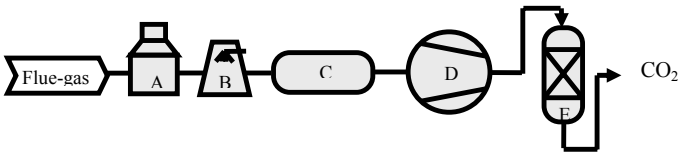

Figure 1 – Process flow diagram of the base case: A – WHSG, B – SO_2 scrubber, C – amine plant, D – CO_2 compressor, E – dehydration unit

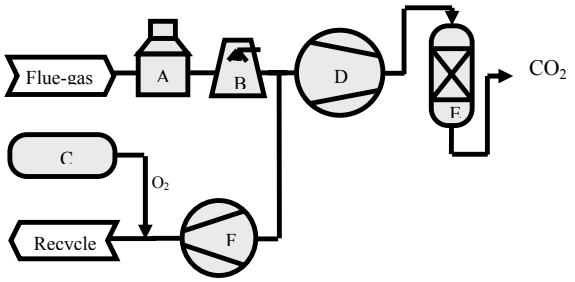

Figure 2 – Process flow diagram of the 99.5%O2 oxyfired case: A – WHSG, B – SO_2 scrubber, C – ASU, D – CO_2 compressor, E – dehydration unit, F – recycle compressor

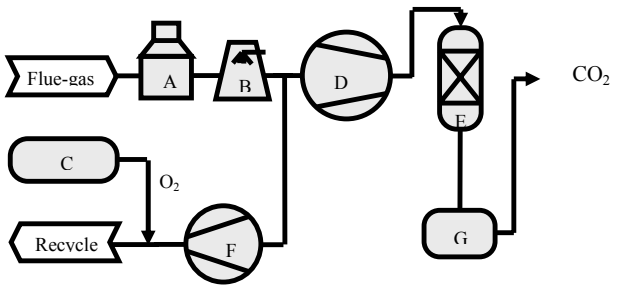

Figure 3 – Process flow diagram of the 95%O2 oxyfired case: A – WHSG, B – SO_2 scrubber, C – ASU, D – CO_2 compressor, E – dehydration unit, F – recycle compressor, G – Propane chillers unit

The chemical requirements cost is mainly associated with limestone needed to react with SO_2 in the SOx scrubber, MEA make-up, corrosion inhibitors, a filter aid to remove particulates, activated carbon to remove hydrocarbons, sodium carbonate to reclaim MEA, molecular sieve replacement in the dehydration systems and disposal costs. The chemical costs were based on prices in the USA (2007) and the consumptions were based on operating 365 days per year. Table 5 shows the relative contribution of each item considered and also the percentage change of the oxyfired cases relative to the base case. The total chemical cost for the oxyfired cases was approximately 77% lower than for the base case and this was mainly due to the chemical requirements associated with the operation of the amine plant.

Table 4 – Utility requirements

	Units	Base case	99.5%O_2	95%O_2
Water makeup	m3/h	67.5	59.8	59.8
Water blowdowns	m3/h	15.1	18.3	18.3
Cooling tower water	m3/d	572.2	288.3	314.1
STEAM CONSUMED				
HP	t/h	140.3	0.3	0.4
MP	t/h	0	2.3	2.4
LP	t/h	216.5	0	0
STEAM PRODUCED (WHSG)				
HP	t/h	78.7	103.6	102.2
Electrical power	MW	15.8	74.0	71.2

Table 5 – Relative chemical requirements cost

	Relative contribution to total chemical cost (% of total)		
	Base Case	**99.5%O_2**	**95%O_2**
MEA	46.8	0	0
Corrosion inhibitor	8.7	0	0
Filter aid	4.9	0	0
Activated carbon	6.9	0	0
Sodium carbonate	8.4	0	0
Disposal costs	21.0	85.5	85.3
Mol sieve	0.5	2.4	2.6
Limestone	2.8	12.1	12.1
	% change relative to base case		
Total cost	-	- 76.9	- 76.8

3.3. Installed costs

Major priced equipment include the total installed costs for the WHSG, the SO_2 scrubber, the amine plant and the oxygen plant. The plant total cost includes equipment cost, material, freight, construction directs, indirects, home office engineering, insurance and profit for the recycle compression system, CO_2 compression system, molecular sieve dehydration system, propane refrigeration system and the balance of plant. The grand total is the sum of the major priced equipments and the plant total. Contingency, escalation and taxes are excluded costs and are not part of the total cost of the project. The costs are at a quality of ±30% based on 2007 pricing. Table 6 shows the relative contribution of each item considered and also the percentage change of the oxyfired cases relative to the base case. The amine plant is responsible for almost 45% of total installed cost in the base case whereas for the oxyfiring cases the ASU unit represents the highest contribution. Nevertheless, the total installed costs for both oxyfiring cases were at least 45% greater than for the base case.

It is important to emphasize that for the oxifired cases, the recycle compressor works as a substitute for the air blower in the base case. Since the current analysis is a “retrofit” of an existing unit, the cost of the blower was not considered in the base case. However, to perform the comparison on the same basis, the operational cost of the air blower was considered by means of the HP steam demand needed for its operation.

Table 6 – Relative installed costs

	Relative contribution to total capital cost (% of total)		
	Base Case	**99.5%O_2**	**95%O_2**
WHSG	11.4	8.4	8.2
SOx Removal	17.8	12.3	12.0
Amine plant	44.9	-	-
ASU		43.0	39.9
Recycle compression	-	10.8	13.0
CO2 compression	9.5	8.7	7.2
Dehydration	3.2	0.9	1.0
Prapane refrigeration	-	-	1.8
Balance of plant	6.9	5.1	5.4
Home office engineering	3.5	6.7	7.0
Insurance	0.3	0.4	0.5
Profit	2.6	3.6	4.0
		% change relative to base case	
Total cost	-	+ 45	+ 48

3.4. CO_2 capture and avoided costs

All the information on utility requirements, chemical requirements cost and installed cost served as the basis to estimate the CAPEX and OPEX and thereafter calculate the CO_2 capture and avoided costs. The following considerations were assumed for the calculations: for the CAPEX estimate, a 20% contingency over total installed cost was assumed; for the OPEX estimate, MP and LP steam were priced at a value that was 23% lower than HP steam, maintenance was estimated as 4% of CAPEX and an operation of 365 days/yr was considered; for the avoided CO_2 cost calculations, typical CO_2 emissions related to steam (0.12 tCO_2/tSteam) and power (0.33 tCO_2/MWh) generation were adopted [3], considering an industrial boiler and a natural gas combined cycle (NGCC) power plant, respectively.

The relative contribution of CAPEX and OPEX to the final CO_2 capture and avoided costs as well as the percentage change of the oxyfired cases relative to the base case can be seen in table 7. For the calculation of captured CO_2, a net steam demand was considered, based on the steam consumed and produced in each case. For the base case, the HP steam consumption in the air blower was considered in the calculations as previously explained.

Both oxyfired cases presented lower CO_2 capture costs than the base case. The best result was presented by the 99.5%O_2 oxyfired case, which showed the lowest CO_2 capture as well as avoided costs. Although oxyfired cases have higher CAPEX than the base case, their lower operational costs compensate for the investment and turn out to give lower capture costs. However, it seems that the significant differences in the final capture cost are associated with the steam and power balance, which represent the main contribution to operational costs. The choice to have newly built motor-driven recycle compressors for the oxyfired cases as opposed to the steam-turbine-driven air blower in the base case certainly exerts a significant influence in such a balance and hence in the final capture cost. For example, a quick estimate on the capture costs considering that the recycle compressor is driven by a steam turbine shows that the difference between the base case and the 99.5%O_2 case would drop from 44% (Table 7) to around 34% (oxyfired case still lower). The difference in capture cost also highly depends on how steam is priced. For instance, if the MP and LP steam values are set to zero, the difference between the base case and the 99.5%O_2 case drops from 44% to 14%. However, the avoided CO_2 cost is still 40% lower for the oxyfired case. Now, if the

steam-turbine-driven recycle compressor case is further considered, then no difference in capture cost between the base case and the 99.5%O_2 case is observed, though there is still a 27% difference for the avoided cost.

Table 7 – Relative capture and avoided costs

	Relative contribution to total cost (% of total)		
	Base Case	**99.5%O_2**	**95%O_2**
CAPEX	18	41	42
OPEX	82	59	58
Total cost		**% change relative to base case**	
Capture	-	- 44	- 38
Avoided	-	- 61	- 56

4. Technical evaluation

Some of the uncertainties associated with operating an FCC unit in the oxyfiring mode are mainly related to the efficiency of catalyst regeneration and its impact on activity and cracking reactions. One of the main concerns is whether CO_2 acts as an inert in typical conditions found in the regenerator. In certain process conditions, the CO_2 molecule may act as an oxidant and react with coke yielding CO, in a shifted Boudouard reaction: $CO_2 + C \rightarrow 2CO$.

In a previous work [4] a series of bench scale experiments were performed to address the mechanisms involved in the combustion of coke under both O_2/He and CO_2/He atmospheres. According to the results, the reaction between CO_2 and coke preferably occurs in the beginning of the process and is influenced by the nature of the coke. It seems that CO_2 reacts more easily with aliphatic species and polysubstituted aromatic species present in the coke. Nevertheless, at typical regenerator temperatures (650 – 720^{o}C) the reaction of CO_2 with coke apparently accounts for less then 5% of total coke burn in the presence o O_2.

4.1. Pilot plant experiments

In another set of experiments, a larger scale test (pilot-plant) was performed where the regeneration of coke was accomplished with O_2 in a CO_2-rich environment to investigate the performance of the regenerator and its operational stability. The main objective was to evaluate the products profile, stability of operation and the effectiveness of coke burn in the regenerator. In this case, two tests were performed at different catalyst-to-oil ratios (9 - 13) at a reaction temperature of 540^{o}C. The gaseous products were quantified by a wet gas flowmeter and its composition was determined by GC analysis. The gaseous compounds are quantified as dry-gas (H_2, C_1- C_2), LPG and gasoline. The total liquid product from the runs was weighted and analyzed by GC SimDist (ASTM2887) and quantified as gasoline (C_5-221^{o}C), light cycle oil (LCO; 221^{o}C-343^{o}C) and bottoms (343+^{o}C). Commercial grades of oxygen and CO_2 were injected into the regenerator to keep the concentration of O_2 at 21% vol.

The main results of the runs operating with air and O_2+CO_2 mixture may be seen in Figures 4a and 4b. No indication of a significant shift in coke yields was observed when the inlet air stream (standard run) was changed to O_2/CO_2 mixture, nor was the activity of the catalyst greatly affected. The use of CO_2 in the regenerator did not substantially change the profile of product slates and it also did not hinder the conversion of coke deposited onto the catalyst surface since the level of coke content in the outlet of the regenerator vessel remained below 0.1 wt.% in either case. Moreover, all operational conditions remained stable throughout the experiments. Despite the fact that the pilot runs were not made with a real CO_2 recycle, the results obtained indicate that it is technically possible to run an FCC unit in the oxyfiring mode while maintaining a stable operation and with no significant impact on catalyst regeneration and activity.

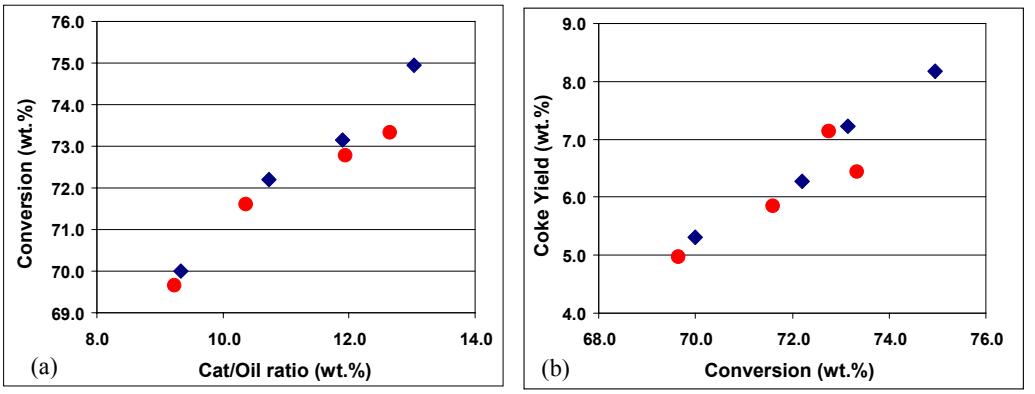

Figure 4 – (a) cat/oil versus conversion and (b) conversion versus coke yield - ♦ Standard (air); ● CO_2+O_2

5. Conclusions

Although the oxyfiring technology showed a higher capital cost compared to the base case, its operational cost was much lower. Since the OPEX contributes more significantly to the final capture cost, the oxyfiring technology showed an approximate 45% and 60% reduction in capture and avoided costs, respectively. However, the differences in the final values seem to be associated with the balance and prices of steam and power, which represent the main contribution to Opex. The choice of motor-driven recycle compressors in the oxyfired cases as opposed to the steam turbine driver of the air blower in the base case certainly had a significant influence in the final costs. Nevertheless, even if the recycle compressors used steam turbine drivers and steam prices were set to zero, the CO_2 avoided cost for the oxyfiring technology would still be lower than for the post-combustion case.

As for the technical evaluation, pilot plant tests were conducted in which a mixture of CO_2+O_2 was used instead of air to regenerate the catalyst. The product profile, stability of operation and the effectiveness of coke burn were evaluated and the results showed no significant changes from normal operation.

Additionally, for the oxyfired cases the CO_2 recycle rate was established to maintain the same volume flow-rate as that of N_2 in air. However, CO_2 has a higher heat capacity than N_2 and this implies that more heat will be removed from the regenerator. For a resid FCC unit that makes use of a cat-cooler this could mean a lower heat duty demand. On the other hand, the "cooling" down effect also opens up the possibility for extra feed processing in the FCC unit. Such possible gains related to the operation in the oxyfiring mode were not taken into account in the present study and may further decrease the CO_2 capture cost. Finally, taking into account the results obtained in this study, the oxyfiring concept has been shown to be an adequate technology for CO_2 capture in FCC units.

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